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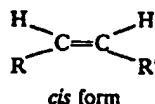
7 Fat eutectics and crystallisation

G. TALBOT

7.1 Glossary of useful terms

cis formation

The C=C double bonds in unsaturated fatty acid chains exist in two conformations – the *cis* formation and the *trans* formation (q.v.). In the *cis* formation, the hydrogen atoms associated with the unsaturated carbon atoms lie on the same side of the double bond, i.e.



Eutectic

When two dissimilar materials are mixed together they can interact in such a way that the melting point of the blend is lower than the melting points of the individual components. This is a eutectic. One of the most commonly encountered eutectics is when salt is sprinkled onto ice. A eutectic is formed with a melting point below that of pure water and the ice will therefore melt.

Fractionation

Naturally occurring oils and fats are mixtures of triglycerides (q.v.) with different melting points. In many fats, some of these triglycerides are solid at room temperature whilst others are liquid. It is possible to separate the liquid triglycerides from the solid triglycerides by a process known as 'fractionation'. Two types of fractionation are commonly employed – dry fractionation and solvent fractionation. In the dry fractionation process, the fat is held at a temperature at which it is partially liquid – the liquid and solid triglycerides are separated by pressing or by filtration. In the solvent fractionation, the fat is dissolved in a solvent – usually acetone or hexane – and the higher melting triglycerides are allowed to crystallise from solution before being separated by a filtration process. The separation efficiency is better with solvent fractionation than with dry fractionation. The melting profiles of the fractions which are

produced are significantly different from those of the starting fat. Palm oil and palm kernel oil are examples of fats which are commonly subjected to fractionation.

Free fatty acid

Triglycerides can undergo hydrolysis (chapter 9) with water, particularly when in the presence of lipase, resulting in the formation of partial glycerides (diglycerides and monoglycerides) together with free fatty acids.

Hydrogenation

Hydrogenation (also known as 'hardening') is a process in which oils and fats are reacted with hydrogen in the presence of a catalyst (usually nickel). During hydrogenation, two competing reactions can take place – saturation in which a hydrogen molecule is added across a double bond of an unsaturated fatty acid group producing a single saturated C—C bond, and isomerisation in which the naturally occurring *cis* double bonds are converted into *trans* double bonds. Both the resulting saturated fatty acids and the *trans* unsaturated fatty acids have a higher melting point than the initial *cis* unsaturated fatty acids – hence the alternative term, 'hardening'.

Isomer

Isomers are alternative distributions of the atoms or functional groups in

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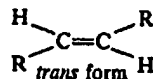
cocoa butter which can exist in six different polymorphic forms, i.e. six different forms of crystal packing.

Saturated fat

Hydrocarbon chains which contain no double bonds are said to be 'saturated'. Fats are made up of triglycerides which in turn are esters of glycerol and fatty acids. If the hydrocarbon chain part of the fatty acids contains no double bonds, then the fat is said to be a 'saturated fat'. Saturated fats or saturated triglycerides are commonly found in oils such as palm kernel oil and coconut oil.

Trans formation

The C=C double bonds in unsaturated fatty acid chains exist in two conformations – the *cis* formation (q.v.) and the *trans* formation. In the *trans* formation, the hydrogen atoms associated with the unsaturated carbon atoms lie on opposite sides of the double bond, i.e.



Triglyceride

Triglycerides are the main chemical species in oils and fats. They are triesters of three fatty acids with the trihydric alcohol, glycerol (see Figure 7.1).

Unsaturated fats

In unsaturated fats, the hydrocarbon chain part of the fatty acids contains one or more double bonds. If there is predominantly one double bond in the fatty acids, then the fat is said to be 'monounsaturated' – olive oil is

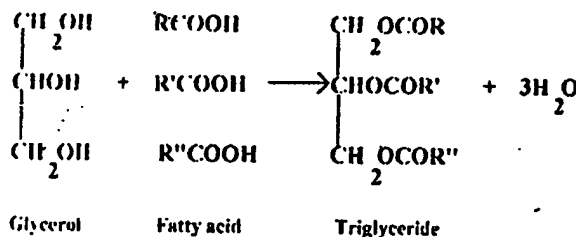


Figure 7.1 Formation of triglycerides. (Reprinted with permission of Loders Croklaan.)

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part of the fatty acids contains
predominantly one double bond in
'monounsaturated' - olive oil is

triglyceride

triglyceride + 3H₂O

triglyceride

triglyceride

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an oil rich in monounsaturated fatty acids. If there is predominantly more than one double bond in the fatty acids, then the fat is said to be 'polyunsaturated' - sunflower oil and soyabean oil are oils rich in polyunsaturated fatty acids.

7.2 Introduction

Fats form a part of almost all fabricated foods and the physical properties of the fat often play an integral part in the production and, in many cases, the consumption of the food. The crystallisation characteristics of the fat phase are of major importance to manufacturers of chocolate, margarine, spreads, coffee whiteners and ice cream, to give but a few examples.

As foods become increasingly complex and multiphase in their construction, so the number of fats used in a given foodstuff increases. The interactions of these fats (which are often considerably different in their melting and crystallisation behaviour) are also of major importance to both manufacturer and consumer.

This chapter considers these aspects from a practical viewpoint. A large amount of fundamental research has, however, been carried out over the years on the interactions of triglycerides of varying degrees of purity. Some of this research has considerable practical significance in that the combinations of triglycerides can be related to 'real-life' fat systems. Other studies are of much more academic interest. This chapter will concentrate almost exclusively on those fat, or triglyceride systems, which have some further relevance to food manufacture or consumption.

7.3 Triglyceride structure

Fats and oils are mixtures of a number of chemical species, which together can loosely be called 'lipids'. These include phosphoglycerides (such as lecithin), partial glycerides (mono- and diglycerides) and free fatty acids, but, in most natural oils and fats, the species present in by far the greatest amounts are triglycerides.

Triglycerides are esters formed by the combination of glycerol and fatty carboxylic acids (Figure 7.1). In most cases, these fatty acids are straight carbon-carbon chains having an even number of carbon atoms, ranging from as few as four carbon atoms (i.e. butyric acid) in butterfat up to ≥ 26 carbon atoms in some fish oils. The common fatty acids found in oils and fats together with their melting points are shown in Table 7.1. It can be seen from this list of acids and their melting points that:

Table 7.1 Fatty acids commonly found in oils and fats

Chain length: double bonds	Systematic name	Trivial name	Melting point	
			°C	°F
10:0	Decanoic	Capric	31.6	88.9
12:0	Dodecanoic	Lauric	44.8	112.6
14:0	Tetradecanoic	Myristic	54.4	129.9
16:0	Hexadecanoic	Palmitic	62.9	145.2
18:0	Octadecanoic	Stearic	70.1	158.2
18:1	Octadec- <i>cis</i> -9-enoic	Oleic	16	60.8
18:1	Octadec- <i>trans</i> -9-enoic	Elaidic	44	111.2
18:2	Octadec- <i>cis</i> -9, <i>cis</i> -12-dienoic	Linoleic	-6.5	20.3
18:3	Octadec- <i>cis</i> -9, <i>cis</i> -12, <i>cis</i> -15-trienoic	Linolenic	-12.8	9.0
20:0	Icosanoic	Arachidic	76.1	169.0

Table 7.2 Melting points of monoacid triglycerides [1]

Triglyceride	Stable (β -form) melting point	
	°C	°F
Trilaurin (LLL)	46	114.8
Trimyristin (MMM)	56	132.8
Tripalmitin (PPP)	66	150.8
Tristearin (SSS)	73	163.4
Triolein (OOO)	5	41.0
Trilaidin (EEE)	41	105.8
Trilinolein (LiLiLi)	-11	12.2

- as the chain length increases so does the melting point;
- the greater the degree of unsaturation (i.e. the more double bonds there are in the fatty acid), the lower the melting point;
- *trans* unsaturated fatty acids have a higher melting point than the corresponding *cis* unsaturated fatty acids.

In many ways, the characteristics of the fatty acids define the properties of the triglycerides of which they are a part. However, because triglycerides contain three fatty acid groups, the physical properties are more complex than those of the more simple fatty acids.

A triglyceride molecule can have all three of its fatty acids the same (monoacid triglycerides), or two can be the same and the third different (diacid triglycerides), or all three can be different (triacid triglycerides).

Monoacid triglycerides are obviously the simplest in the sense that their melting behaviour basically follows the 'rules' of the fatty acids (see Table 7.2). Diacid triglycerides are more complex and can exist as two distinct isomers: RRR' and $RR'R$ (where R and R' are the two fatty acid chains).

and fats

Trivial name	Melting point	
	°C	°F
Capric	31.6	88.9
Lauric	44.8	112.6
Myristic	54.4	129.9
Palmitic	62.9	145.2
Stearic	70.1	158.2
Oleic	16	60.8
Elaidic	44	111.2
Linoleic	-6.5	20.3
Linolenic	-12.8	9.0
Arachidic	76.1	169.0

monoacid triglycerides (1)

Stable (β -form) melting point	
°C	°F
46	114.8
56	132.8
66	150.8
73	163.4
5	41.0
41	105.8
-11	12.2

the melting point;
 (i.e. the more double bonds
 the melting point;
 a higher melting point than the
 provide.

the fatty acids define the properties
 are a part. However, because tri-
 groups, the physical properties are
 simple fatty acids.

all three of its fatty acids the same
 on the same and the third different
 the different (triacid triglycerides).

the simplest in the sense that their
 rules of the fatty acids (see Table
 and can exist as two distinct
 are the two fatty acid chains).

Triacid triglycerides can then obviously exist as an even greater number of isomers:

- (a) $RR'R''$ (b) $R'RR''$ (c) $R''RR'$
 (d) $RR''R'$ (e) $R'R''R$ (f) $R''R'R$

These forms show that chirality or optical isomerism can exist in triglycerides, i.e. forms (a) and (f), (b) and (d), (c) and (e) are pairs of optical isomers. Indeed the asymmetrical diacid triglyceride RRR' can also exist as a pair of optical isomers (RRR' and $R'RR$).

7.4 Molecular packing of triglycerides

The basic structure of a triglyceride molecule can be likened to a chair and these chair structures can pack together in a crystal lattice in two basic ways, i.e. double-chain length and triple-chain length packing (Figure 7.2).

Triple-chain length structures are found in the symmetrical mono-unsaturated triglycerides (POP, POST, StOST – see section 7.5.1) found in the more stable polymorphic forms of cocoa butter (the fat produced by pressing the cotyledons in cocoa beans). They also exist in saturated triglycerides in which the chain lengths of the fatty acids differ by four carbon atoms or more.

The crystalline structure of fats is complicated further by the phenomenon of polymorphism, i.e. the ability of a fat to crystallise in a number of forms with different types of molecular packing and different thermodynamic stabilities. Four basic polymorphic forms exist in fats – known as sub- α , α , β' and β – although some fats, notably cocoa butter, exhibit more than four polymorphs. The extra structures are, however, generally variants of the four basic forms. The sub- α form is the most transient and least stable of these forms and, in practical applications, the remaining three forms are the most important. The various forms can be distinguished by X-ray diffraction and this method is also used to determine whether the fat crystals are packed in double- or triple-chain lengths

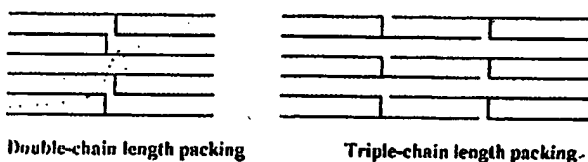


Figure 7.2 Double- and triple-chain length packing configuration. (Reprinted with permission of Lodders Crokiaan.)

(Figure 7.3). The polymorphic form of a fat is found from its X-ray short spacings (S) whilst the type of chain packing is determined by its X-ray long spacings (L). This is approximately 50% longer for triple-chain packed systems compared with double-chain packed systems. The X-ray short spacings which define the various polymorphic forms are listed in Table 7.3.

The basic structures of the three main polymorphs are shown in Figure 7.4. Triglycerides in the α -form also have their fatty acid chains parallel with each other and perpendicular to the end plane, but, relative to each other, the chains are less ordered than the sub- α form (see below) and when viewed end on, have a more hexagonal configuration, similar to a clump of pencils.

The β' form exists in the form of an O_L sub-cell, but, unlike the sub- α form (see below), the fatty acid chains are no longer perpendicular to the end plane, but are inclined.

In the β form, the fatty acid chains are inclined at an angle to the end plane, but differ from the β' form in that all the fatty acid chains are parallel to each other forming a triclinic (T_{\parallel}) sub-cell.

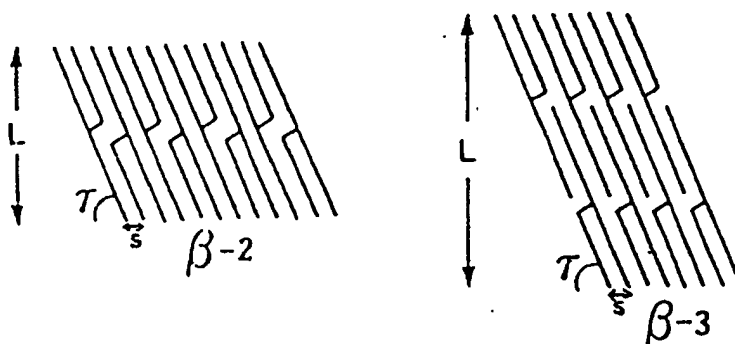


Figure 7.3 X-ray diffraction - long and short spacing. (Reprinted with permission of Lodders Crokiaan.)

Table 7.3 Assignment of polymorphs [7]

Polymorph	X-ray short spacing characteristics
α	A single, strong, short spacing at about 0.415 nm
β'	Usually two, strong, short spacings at about 0.38 nm and 0.42 nm or three, strong, short spacings at about 0.427 nm, 0.397 nm and 0.371 nm
β	A form which does not satisfy the criteria for α and β' , but also usually shows a very strong short spacing at about 0.46 nm
sub- α	A β' form usually melting below an α form

a fat is found from its X-ray short spacing is determined by its X-ray spacing is approximately 50% longer for triple-chain systems. The X-ray spacings for the polymorphic forms are listed in Table 7.1.

The polymorphs are shown in Figure 7.4. In the α form, the fatty acid chains are parallel to the end plane, but, relative to each other, they are in the sub- α form (see below) and in a hexagonal configuration, similar to a

sub-cell, but, unlike the sub- α form, the fatty acid chains are no longer perpendicular to the

planes. In the β form, the fatty acid chains are inclined at an angle to the end plane. In the β' form, all the fatty acid chains are perpendicular to the end plane.

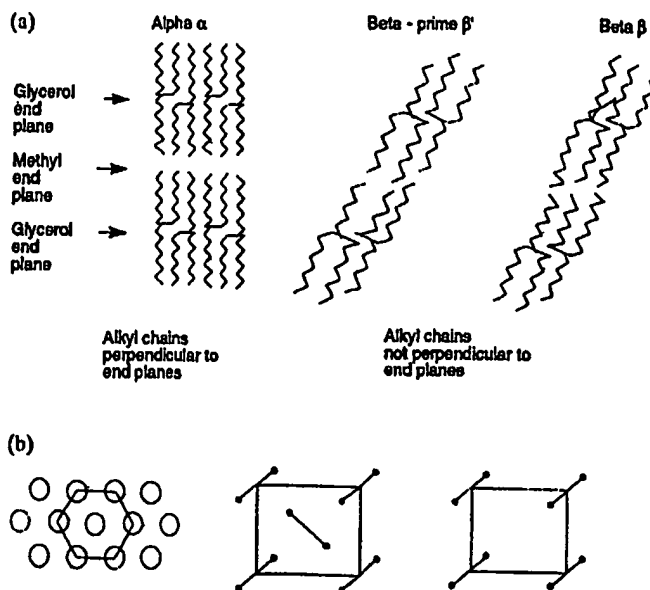


Figure 7.4 Structure of main polymorphic forms. (a) Projection showing arrangement of alkyl chains for α , β and β' polymorphs. (b) Projection parallel to direction of alkyl chain (i.e. arrangement looking onto ends of chains). (Reprinted with permission of Lodders Crokiaan.)

In the sub- α form (not shown in Figure 7.4), the fatty acid chains are perpendicular to the planes defining layers of glycerides whilst, looking end on to the glyceride chains they form an orthorhombic sub-cell in which the fatty acid chains of adjacent triglycerides are mutually perpendicular (the O_1 sub-cell). In this respect, this is similar to the β' configuration. Indeed, some workers have considered the sub- α form to be a variant of the β' form.

It has already been mentioned that cocoa butter can exist in six different polymorphic forms. These include two β' and two β forms. The most stable form of each pair is given the suffix 1 and the least stable the suffix 2, i.e. β'_2 has a lower stability than β'_1 .

7.5 Composition and structure of natural fats

The remainder of this chapter will concentrate on natural fats commonly used in foodstuffs and will firstly relate their triglyceride composition to their polymorphism and crystallisation characteristics and then discuss the interactions which occur when fats are mixed together.

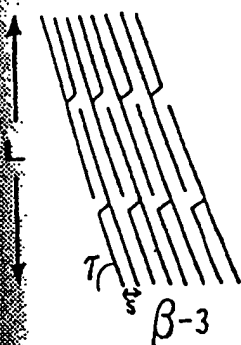


Fig. (Reprinted with permission of

Table 7.1

Polymorphic form	Characteristics
α	0.415 nm
β	About 0.38 nm and 0.42 nm or three, 0.397 nm and 0.371 nm
β'	0.397 nm and 0.371 nm
β_1	0.397 nm and 0.371 nm
β_2	0.397 nm and 0.371 nm
β_3	0.397 nm and 0.371 nm
β_4	0.397 nm and 0.371 nm
β_5	0.397 nm and 0.371 nm
β_6	0.397 nm and 0.371 nm

7.5.1 Cocoa butter

The extensive polymorphism of cocoa butter has already been referred to. Wille and Lutton [2] defined the six polymorphic forms as Forms I to VI and this nomenclature is often used by chocolate and confectionery technologists. The relationship between these six forms and the nomenclature, used earlier in this chapter for polymorphic forms, is shown in Table 7.4 where Wille and Lutton's Forms I to VI are compared with those defined by Larsson [3].

The thermal characteristics of Forms I to V have been determined by DSC (differential scanning calorimetry) heating curves [4].

Form I. This was produced by heating cocoa butter at 100°C (212°F) for 2 minutes before quenching to 0°C (32°F). The fat was immediately heated at 5°C/min (9°F/min) to 40°C (104°F).

Form II. This was produced in much the same way as Form I except that the fat was held at 0°C (32°F) for 15 minutes before measuring the DSC heating curve (5°C/min to 40°C; 9°F/min to 104°F) to allow transformation from Form I.

Form III. This was produced by quenching from 100°C to 5°C (212°F to 41°F) and then holding at 5°C (41°F) for 16 hours. After holding at 0°C (32°F) for a further 5 minutes, the DSC heating curve was measured.

Form IV. This was produced by quenching from 100°C (212°F) to 16°C (60.8°F), holding there for 1 hour and then to 10°C (50°F) for 15 minutes before measuring the DSC curve. This is akin to taking a liquid cocoa butter and putting it through a normal chocolate cooling regime without prior tempering (see chapter 17).

Form V. This was produced by incubating at 20°C (68°F) for 11 days. After holding at 18°C (64.4°F) for 5 minutes, the DSC curve was measured. Properly tempered chocolate produces Form V crystals in the cocoa butter.

Form VI. This needs several months at 20°C (68°F) before it forms.

Table 7.4 Polymorphic forms of cocoa butter

Wille and Lutton [2]	Larsson [3]*	Melting point		Chain packing
		°C	°F	
Form I	β'_2	16-18	61-67	Double
Form II	α	21-22	70-72	Double
Form III	Mixed	25.5	78	Double
Form IV	β'_1	27-29	81-84	Double
Form V	β_2	34-35	93-95	Triple
Form VI	β_1	36	97	Triple

* Suffixes 1 and 2 are used to indicate highest and lowest melting form with similar crystal packing.

has already been referred to the polymorphic forms as Forms I to V in chocolate and confectionery. The forms and the nomenclature used for them, is shown in Table 7.1. They are compared with those of the other forms.

have been determined by DSC heating curves [4].

butler at 100°C (212°F) for 10 hours. The fat was immediately cooled to 10°C (50°F) to allow trans-

formation as Form I except that before measuring the DSC heating curve, the sample was held at 10°C (50°F) to allow trans-

formation from 100°C (212°F) to 5°C (41°F) for 10 hours. After holding at 0°C (32°F) for 10 hours, the DSC heating curve was measured.

From 100°C (212°F) to 16°C (61°F) for 15 hours. This is akin to taking a liquid chocolate cooling regime.

at 20°C (68°F) for 11 days. After this, the DSC curve was measured. This produces Form V crystals in the sample.

(10°C) before it forms.

Form	Chain packing
I	Double
II	Double
III	Double
IV	Double
V	Triple
VI	Triple

Form with similar crystal

The DSC heating curves of Forms I to V are shown in Figure 7.5. As the stability of the cocoa butter increases (from Form I to Form V) so the melting point of the fat increases. The maximum melting points as measured by DSC heating curves increase from 19.75°C (67.55°F) (Form I) to 33.37°C (92.06°F) (Form V). Other observations have shown that a polymorphic change from Form V to Form VI increases the melting point

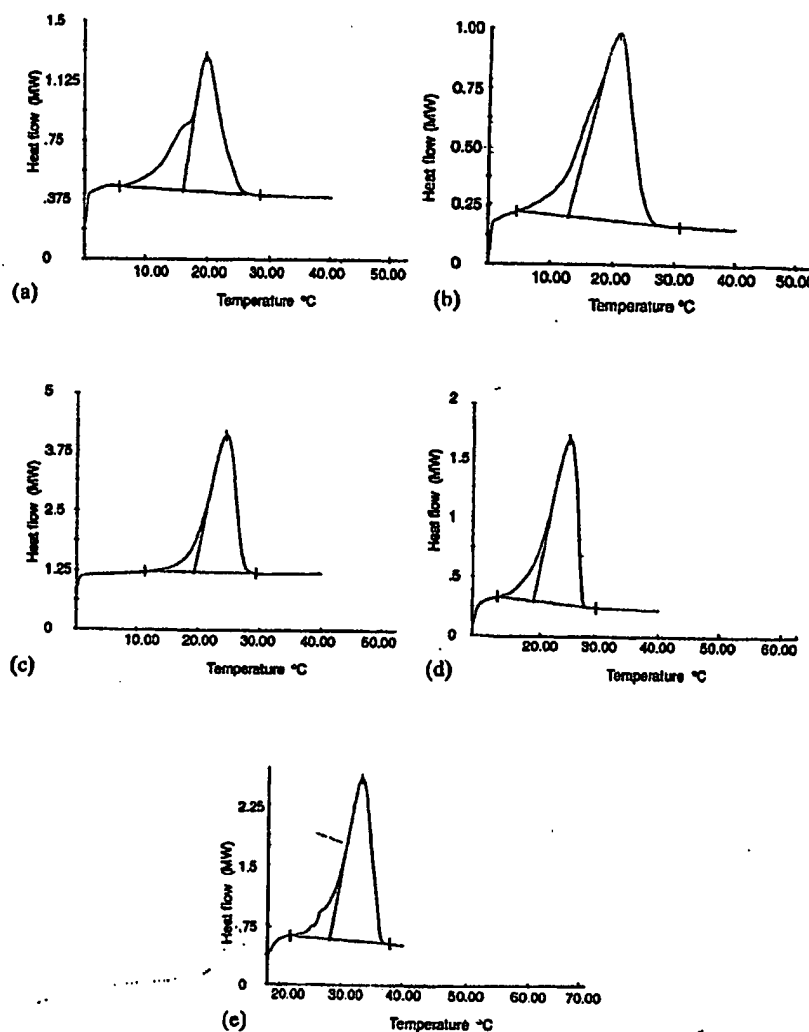


Figure 7.5 DSC heating curves of Forms I to V of cocoa butter. (Reprinted with permission of Loders Crocklaan.)

by approximately 2°C (4°F). This polymorphic change and further increase in melting point is often the cause of what is considered to be 'staling' in chocolate which has been stored for a few months. This polymorphic change from Form V to Form VI also results in a change in the crystal structure of cocoa butter which can result in crystals of fat forming on the surface of the chocolate. These have the appearance of mould and are known as 'chocolate bloom'.

Cocoa butter, unlike many other naturally occurring fats, has a relatively simple triglyceride composition. In many cocoa butters, three triglycerides comprise well over 80% of the total. These triglycerides are POP, POSt and StOSt (P = palmitic, St = stearic, O = oleic). These are physically and chemically very similar and might be expected to interact in a predictable, linear fashion. Andersson [5], however, calculated the ternary phase diagram of POP-POSt-StOSt mixtures (Figure 7.6) and showed that there are non-linear interactions between the three triglycerides. The shaded areas show regions where the melting points are reduced below the melting points of the individual triglycerides. At a composition of about 10% StOSt, 40% POSt and 50% POP, a eutectic (*see glossary*) is formed with a melting point of 33.8°C (92.8°F). The ratio of POP:POSt:StOSt found in cocoa butter is shown as point K in Figure 7.6. There are other soft triglycerides in cocoa butter which bring the melting point down below this figure.

Thus, even very similar triglycerides interact in such a way that eutectics

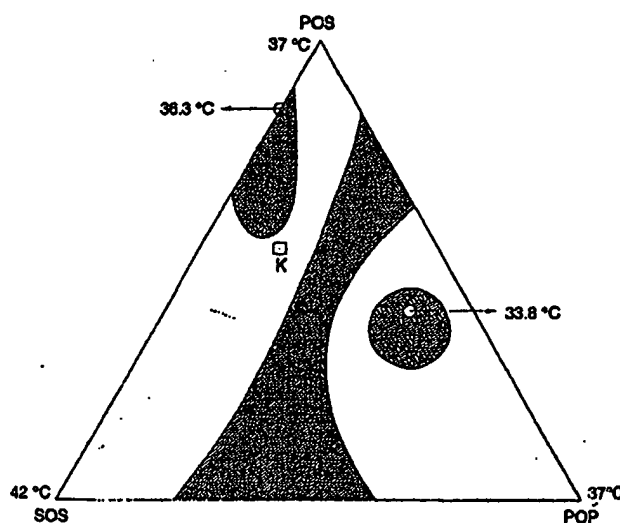


Figure 7.6 POP-POSt-StOSt ternary diagram [5].

morphic change and further increase what is considered to be 'staling' in a few months. This polymorphic results in a change in the crystal structure in crystals of fat forming on the surface, the appearance of mould and are

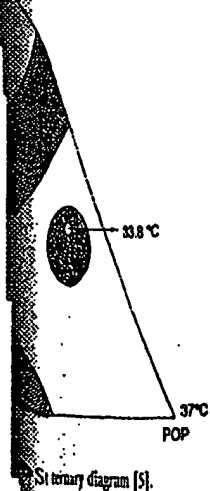
naturally occurring fats, has a relatively small number of triglycerides. In cocoa butters, three triglycerides are POP, POST, and STOST (O = oleic). These are physically expected to interact in a pre-arranged manner, however, calculated the ternary phase diagrams (Figure 7.6) and showed that the melting points are reduced for individual triglycerides. At a composition of 50% POST and 50% POP, a eutectic (see Figure 7.6) is shown as point K in Figure 7.6 in cocoa butter which bring the

interact in such a way that eutectics

are formed. Other triglycerides found in cocoa butter, albeit in smaller quantities, can also have a drastic effect, particularly on crystallisation. When chocolate is processed it is tempered to ensure that the cocoa butter crystallises in a stable polymorphic form (Form V). The major triglycerides in cocoa butter (POP, POST, STOST), collectively known as 'SOS' (S = saturated), are usually the highest melting triglycerides and hence crystallise sufficiently during the tempering process to 'seed' the remaining cocoa butter in the same stable polymorphic form. If, however, the cocoa butter also contains some trisaturated triglycerides, then these, being higher melting, will crystallise before the SOS triglycerides. Because these 'extra' crystals effectively reduce the amount of cocoa butter remaining in the liquid phase, the viscosity of the tempered chocolate is increased [6].

The generation of 'seeds' during crystallisation is an important step, whatever the fat, since the rate determining step in a crystallisation process is often the nucleation stage. Classical tempering of chocolate relies on temperature changes firstly to generate both stable β (Form V) and unstable β' (Form IV) polymorphs by cooling below the β' melting point. This is followed by heating to a temperature between the melting points of the two polymorphic forms in order to leave only stable β (Form V) crystals to 'seed' the bulk of the chocolate. Cocoa butter (and hence chocolate) can, however, also be tempered by the external addition of stable β SOS seeds [21]. Because the amount of seed and the polymorphic integrity of the seed can be better controlled than by the cooling-reheating process, this would then be a more robust method of tempering. Higher melting SOS triglycerides, e.g. BOB (B = behenic), have been used in chocolate as a way of reseeded tempered chocolate products which, because of climatic extremes, have melted on storage [22]. This is claimed to improve the heat stability of the product.

Where an unsaturated fatty acid (e.g. oleic acid) is present in a triglyceride chain, there is an angular change in the carbon-carbon chain at the unsaturated carbon-carbon bond. However, it has been shown by de Jong *et al.* [8] that oleic acid can exist in a number of conformations, all of which show this angular change at the double bond. One conformation, in particular, has a further rotation around an adjacent carbon-carbon single bond giving an overall fatty acid chain showing much greater linearity than was previously considered possible in oleic acid (Figure 7.7). It has been hypothesised from these data [9] that the oleic acid chain in cocoa butter in Form V has the 'straight-chain' oleic acid and that this transforms slowly into the 'bent-chain' configuration producing Form VI cocoa butter. To prevent this transformation, a triglyceride which crystallises in a straight-chain, triple-packed, β -configuration can be introduced into the cocoa butter crystal lattice. This is the basis of a patented product ('Prestine' from Loders Crokiaan) which prevents the



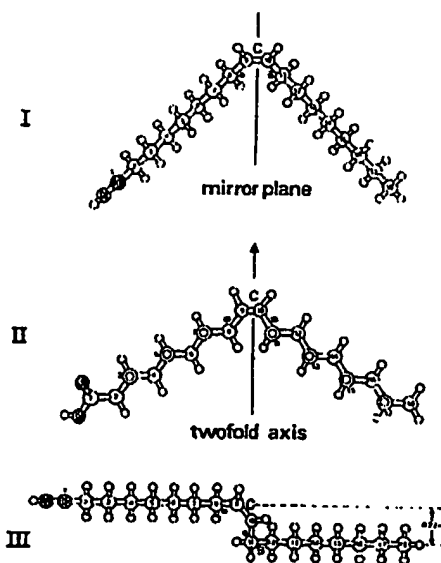


Figure 7.7 Alternative conformations of oleic acid [8].

Form V to Form VI change and hence staling and bloom formation in chocolate [10].

7.5.2 Milk fat

The crystallisation characteristics of milk fat are clearly of importance to the dairy industry in general and butter-making in particular. The phase behaviour has been studied in depth by Timms [11,12] who showed that triglycerides in milk fat can be divided into three broad groups based on their melting points. He called these HMF (high melting), MMF (middle melting) and LMF (low melting) fractions. The DSC heating curve of milk fat shows three distinct peaks which correspond broadly to these three fractions. The low-melting fraction is normally liquid at ambient temperatures and acts as a solvent for the other two fractions. The two solid fractions differ, however, in their polymorphism with HMF being β -stable and MMF being β' -stable. Both fractions exhibit double chain length packing.

7.5.3 Palm oil

Because of its commercial importance in a wide range of foods, palm oil is probably one of the most characterised oils in terms of its triglyceride composition (Table 7.5). If palm oil is cooled rapidly from liquid to

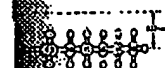
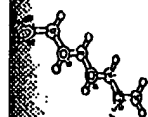
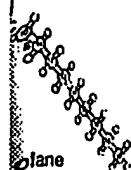
Table 7.5 Triglyceride composition of Sumatran palm oil [11]

Saturated		Mono-unsaturated		Di-unsaturated		Tri(+)unsaturated	
PPP	6.1	MOP	1.3	POO	18.9	OOO	3.2
PPSt	0.9	POP	25.9	StOO	2.6	POLi	2.6
Others	1.5	POST	3.1	OPO	1.2	PLiO	4.3
		PPO	6.0	PLiP	6.8	Others	8.5
		Others	1.6	PLiSt	1.9		
				Others	3.6		

–15°C (5°F) a sub- α polymorph is produced [12]. Reheating to –10°C to –5°C (14°F to 23°F) results in a transformation to an α form. Further heating to between 5°C and 7°C (41°F and 45°F) gives a β' form. In practice, palm oil is not subjected to the drastic cooling necessary to generate the sub- α form, but the more stable polymorphs are important in, for example, margarine production.

Palm oil can also be fractionated using either dry fractionation or solvent fractionation (*see glossary*) [13]. Usually three fractions are collected (although dry fractionation processes are often used to produce only palm oleine and palm stearine). These fractions result in a concentration of the trisaturated triglycerides (PPP etc.) in the 'top fraction', disaturated triglycerides (POP, POST, PLiP; PPO Li = linoleic) in the 'mid-fraction' and the more unsaturated triglycerides (POO, OOO etc.) in the 'oleine fraction'. Monoacid saturated triglycerides such as PPP and, indeed, those trisaturated triglycerides where the fatty acid chain lengths differ by two carbon atoms (i.e. PPSt, StPP) have the β_{-2} form as their stable polymorph. Since, in many applications, the oleine fraction is liquid in use, its polymorphism is perhaps less critical, although it has been shown to proceed from sub- α through α to a β' form. The mid-fraction is perhaps the most interesting fraction in terms of crystallisation and polymorphism, partly because of the combinations of triglycerides in that fraction and partly because of its use as a constituent of cocoa butter equivalents (section 7.7.2 [14]). It has been shown that palm mid-fraction produced by acetone fractionation of palm oil normally crystallises in the β_{-2} form.

The major triglycerides in palm mid-fraction are POP and POST with smaller but significant levels of PPO, PPP and PLiP. Rossell, in his review of phase diagrams of triglyceride systems [15], considers the phase diagrams of binary mixtures of triglycerides such as these. Of importance in the context of palm mid-fraction are POP–PPP, POP–POST and POP–PPO. As is often the case where triglycerides of widely different melting points are studied, the POP–PPP system is essentially monotectic. The POP–POST binary system shows a eutectic composition at about 30% POP and Rossell [15] also suggests the probability that a two-phase



axis of oleic acid [8].

tail and bloom formation in

are clearly of importance to
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 [11,12] who showed that
 three broad groups based on
 (high melting), MMF (middle
 The DSC heating curve of
 correspond broadly to these
 normally liquid at ambient
 other two fractions. The two
 polymorphism with HMF being β
 actions exhibit double chain

wide range of foods, palm oil
 in terms of its triglyceride
 cooled rapidly from liquid to

region exists between 15% and 45% POP. This region is removed from the POP-POSt composition found in palm mid-fraction. Finally the POP-PPO system has been extensively studied by Moran [16], Rossell [17] and Timms and Bessell [18]. Moran [16] showed a eutectic composition at 15–22% POP. Timms and Bessell [18] showed that compound formation occurred with POP-PPO blends. POP in the β'_2 form and PPO in the β'_3 form produced a polymorphically stable compound in the β_2 form. From this and other similar binary studies, Timms formulated conditions under which compound formation occurred [7]:

- There should be a mixture of symmetrical and asymmetrical mono-unsaturated triglycerides.
- The symmetrical triglyceride should contain only one sort of saturated acid.
- The asymmetrical triglyceride may contain two different saturated acids provided that the acid common to both glycerides forming the compound is at the 2-position.

When these conditions are fulfilled, the fatty acid chains pack to give three identical acids side by side.

7.5.4 *Palm kernel and coconut oils*

Both palm kernel oil and coconut oil are rich in lauric acid (approximately 50% in both cases) and the predominant triglyceride is trilaurin. Trilaurin is one of the few triglycerides on which single-crystal X-ray studies have been carried out [19]. These studies showed that pure trilaurin crystallises in the β form. X-ray studies on palm kernel oil and coconut oil products, however, have shown these to be β'_2 -stable. It is also known that there is a relationship between crystallisation rate and fatty acid chain length – the shorter the chain length, the faster the crystallisation rate [13]. Thus lauric fats, such as these, will crystallise more rapidly than their non-lauric counterparts. Since fast crystallisation also gives smaller crystals, the end result is a fat containing small β' crystals. This makes them ideal for use in analogues of whipped dairy products, such as toppings and non-dairy creams, where these types of crystals provide the greatest surface area to stabilise the whipped system.

7.5.5 *Animal fats*

The main animal fat used in food products is probably butterfat (milk fat); this has already been considered in section 7.5.2. Carcass fats such as tallow and lard are less widespread in their use, especially with consumer trends towards vegetable fats on the grounds of healthier nutrition. Their polymorphism is quite complex with beef tallow being mainly β'_2 with a

This region is removed from the mid-fraction. Finally the study by Moran [16], Rossell [16] showed a eutectic composition. [18] showed that compound POP in the β' - β_2 form and is a kinetically stable compound in the early studies, Timms formulated that it occurred [7]:

Equal and asymmetrical mono-

in only one sort of saturated

two different saturated acids
triglycerides forming the com-

monofatty acid chains pack to give

lauric acid (approximately 12 carbons) triglyceride is trilaurin. Trilaurin crystal X-ray studies have shown that pure trilaurin crystallises in the β_2 form and coconut oil products, it is also known that there is a relationship between fatty acid chain length - crystallisation rate [13]. Thus shorter chain lengths crystallise more rapidly than their non-saturated counterparts, so gives smaller crystals, which is ideal for products such as toppings and non-fat spreads to provide the greatest surface area.

Probably butterfat (milk fat).
5.2. Carcass fats such as those from beef, especially with consumer interest in healthier nutrition. Their composition is being mainly β' - β_2 with a

small amount of β (possibly from POP-PPO compound formation). At ambient temperatures, lard is composed of both β and β' crystals, the latter probably from the StPO triglyceride. When heated to 31°C (87.8°F), lard transforms into a pure β phase [20].

7.5.6 Hydrogenated fats

Fats can either be hydrogenated to completion, in which all the unsaturated bonds are converted to saturated bonds, and hence only tri-saturated triglycerides are present, or they can be partially hydrogenated, in which case some of the *cis* unsaturated bonds will also be converted to *trans* unsaturated bonds. Apart from a few specialised applications (stabilisers, hardstocks for spreads and margarines) the only fats which are extensively used in a fully hydrogenated form are palm kernel oil and coconut oil. This is simply because longer chain oils (palm oil, soyabean oil, etc.), when fully hydrogenated, have a melting point which is greatly in excess of mouth temperature. The crystallisation characteristics of fully hydrogenated lauric oils are essentially the same as those already referred to in section 7.5.4, i.e. their stable polymorphic form is the β_2 form.

The presence of *trans*-fatty acids, such as elaidic acid in partially hydrogenated fats, does tend to complicate their polymorphism, but again they have a tendency to crystallise in the β' - β_2 form.

7.6 Mixtures of fats and eutectic effects

Mixtures of fats in food products are usually there deliberately, because they impart some functionality to the product, but they can also occur as a result of fat migrating from one part of the product to another. In the increasingly complex multiphase structure of foodstuffs of today, this 'migration mixing' is becoming more of a problem.

This mixing of fats can often result in the formation of a eutectic composition. The simplest definition of a eutectic composition is one which has a melting point below that of the components making up the mixture. Reference has already been made to eutectics occurring in binary mixtures of triglycerides and there are many more examples where blending of fats can result in melting points below those of the constituent fats. It has also been shown already that different fats have differing polymorphic stabilities and blending of these, whether deliberate or because of migration, can then result in polymorphic instabilities, phase separation, etc.

Although all fats exhibit polymorphism to some extent, particularly when shock-cooled to low temperatures and then allowed to warm up, it is fats like cocoa butter and the constituent fats of cocoa butter equivalents

(palm oil, shea butter, illipe) which have been considered to be 'polymorphic'. These all have the property of being β -stable. Other fats (lauric fats, hydrogenated fats, etc.) are much easier to crystallise into a stable polymorphic form, and in fact do so to such an extent that they have been labelled 'non-polymorphic' but are more accurately called β' -stable. Of this latter group, fats based on lauric oils (palm kernel and coconut) and fats resulting from hydrogenation of liquid oils (palm, soyabean, rapeseed, etc.) also behave quite differently and, despite their polymorphic similarities, can also give crystal structure 'problems' when mixed together.

Thus, in very simple terms, we can divide fats into three main groups:

1. β -stable fats which need tempering (cocoa butter, cocoa butter equivalents).
2. β' -stable, non-lauric fats (hydrogenated palm, soyabean, rapeseed oils).
3. β' -stable lauric fats (palm kernel, coconut oils).

In the following section we will consider the interactions between fats from these three groups when they are blended with each other.

7.7 Blends with β -stable fats

Since the most common 'polymorphic' fat is cocoa butter and, indeed, most work has been done with cocoa butter, this section will consider the effects of blending other fat systems with cocoa butter.

7.7.1 Cocoa butter-milk fat

This is the basis of milk chocolate and, as a consequence, has been extensively studied. The melting profiles of blends of cocoa butter and milk fat are shown in the form of an iso-solids diagram in Figure 7.8. This type of diagram joins points on a composition-temperature diagram with equal solid fat contents. If the lines are parallel and approximately horizontal, then the two components exhibit good compatibility. It is quite obvious from Figure 7.8 that this is not the case with cocoa butter-milk fat blends. Even small amounts of milk fat soften cocoa butter quite dramatically. For example, the solid fat content at 20°C (68°F) of cocoa butter is about 75%. When 20% milk fat is added to the cocoa butter, the solid fat content drops to <60%. Many milk chocolates contain this amount of milk fat (calculated on the fat phase). The reasons for this sharp reduction in solid fat content are two-fold:

- milk fat is in itself a softer fat than cocoa butter and therefore addition (as with any soft fat) will reduce the amount of solid fat present, and

been considered to be 'polymorphic β -stable. Other fats (lauric) easier to crystallise into a stable form to such an extent that they have been more accurately called β' -stable. Of liquid oils (palm kernel and coconut) and of liquid oils (palm, soyabean, rapeseed and, despite their polymorphic structure 'problems' when mixed

divide fats into three main groups: (1) cocoa butter, cocoa butter equivalents (cocoa butter, cocoa butter equivalents, palm, soyabean, rapeseed and coconut oils).

Consider the interactions between fats blended with each other.

If fat is cocoa butter and, indeed, if it is not, this section will consider the interactions between cocoa butter.

As a consequence, it has been found that blends of cocoa butter and cocoa butter equivalents (CBEs) show an iso-solids phase diagram in Figure 7.8. This composition-temperature diagram shows that the two fats are fully compatible with each other. It is not the case with cocoa butter-milk fat. In this case, the lines are generally parallel and horizontal showing that the two fats are fully compatible with each other. Because CBEs contain the same triglycerides as cocoa butter, they also exhibit the same polymorphism and crystallisation behaviour. Thus, all combinations of cocoa butter and Coberine crystallise in a β_3 (Form V) crystal form and no eutectic is observed.

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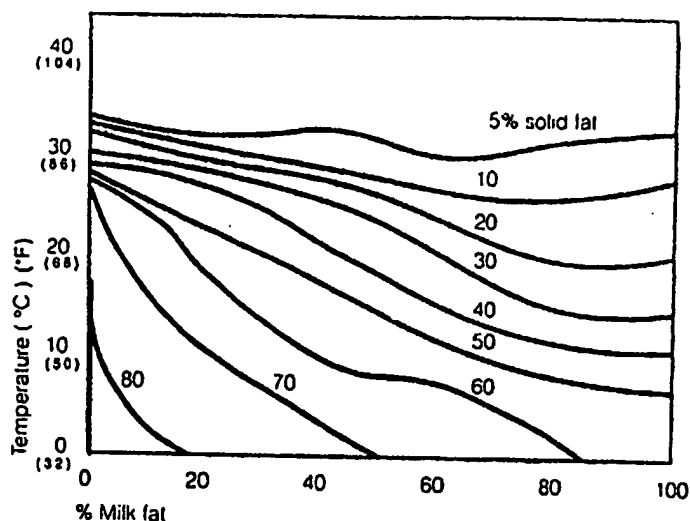


Figure 7.8 Iso-solids phase diagram of cocoa butter-milk fat. (Reprinted with permission of Loders Crokiaan.)

- the triglycerides in milk fat exhibit a different crystal structure to that found with cocoa butter.

7.7.2 Cocoa butter-cocoa butter equivalent

Cocoa butter equivalents (CBEs) are commercially available vegetable fats which contain the same basic triglycerides – POP, POST and StOST – as are present in cocoa butter. The iso-solids phase diagram for blends of cocoa butter with a typical CBE, Coberine, is shown in Figure 7.9 (from [23]). In this case, the lines are generally parallel and horizontal showing that the two fats are fully compatible with each other. Because CBEs contain the same triglycerides as cocoa butter, they also exhibit the same polymorphism and crystallisation behaviour. Thus, all combinations of cocoa butter and Coberine crystallise in a β_3 (Form V) crystal form and no eutectic is observed.

7.7.3 Cocoa butter-lauric fats

Substitute chocolate can be produced from lauric fats, particularly hydrogenated and/or fractionated palm kernel oil. In order to make this look and taste like chocolate, cocoa powder (ground cocoa beans with the majority of the cocoa butter removed) is used in the composition. This also contributes some cocoa butter to the total coating and so the inter-

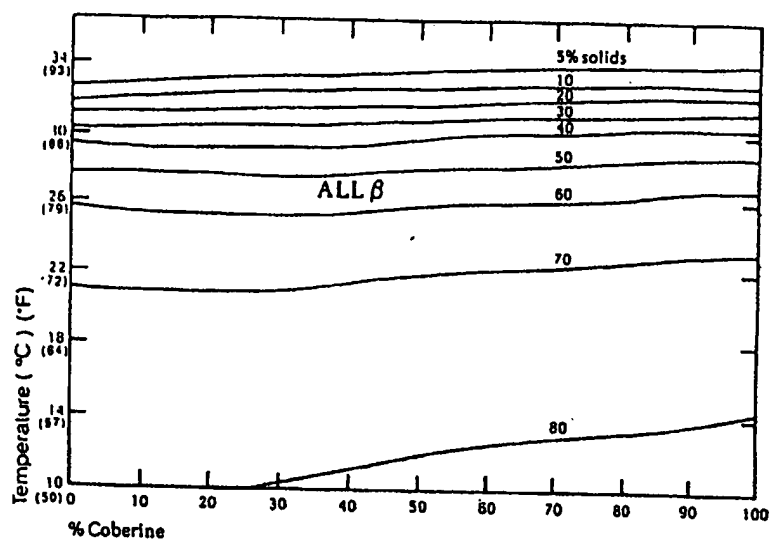


Figure 7.9 Iso-solids phase diagram of cocoa butter-Coberine (CBE). (Reprinted with permission of Loders Croklaan.)

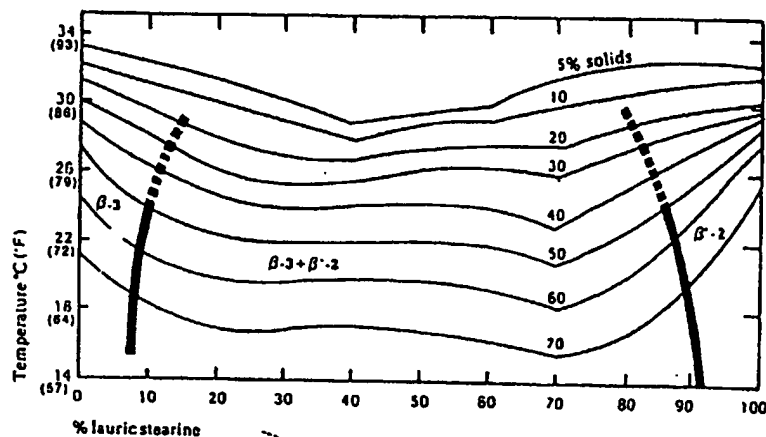


Figure 7.10 Iso-solids phase diagram of cocoa butter-lauric fat. (Reprinted with permission of Loders Croklaan.)

action between cocoa butter and lauric fats becomes important. The iso-solids phase diagram of this system is shown in Figure 7.10 (from [23]). It has already been noted that cocoa butter crystallises in a stable β_{-3} structure and lauric fats in a stable β'_{-2} structure. When either of

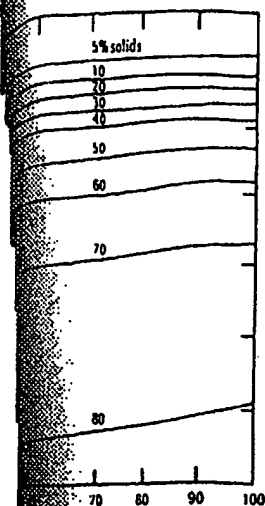


Figure 7.10 Iso-therms (CBE). (Reprinted with permission of Loders Croklaan.)

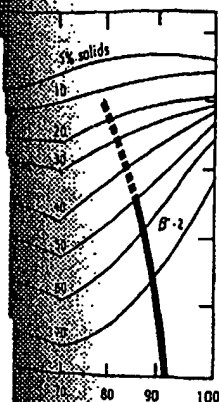


Figure 7.11 Iso-therms (CBE). (Reprinted with permission of Loders Croklaan.)

these fats predominates in the composition, the crystal structure will be dictated by the predominant fat. However, when ca. <95% of the predominant fat is present, a mixed-crystal system is observed, which not only shows crystal instability but also considerable softening.

7.7.4 Cocoa butter-hydrogenated fats

Substitute chocolate coatings can also be produced from hydrogenated non-lauric oils (e.g. palm, soyabean, cottonseed). The iso-solids phase diagram of this system is shown in Figure 7.11 (from [23]). There are some similarities with the cocoa butter/lauric fat system in that:

- Both the lauric fat and the hydrogenated fat have a stable β'_2 crystal structure.
- There is an unstable mixed-crystal structure when neither fat is predominant.
- Softening is observed when one fat is added to the other, although this is not as great as with the lauric fat system.

The main difference between the two systems is that, with the cocoa butter-hydrogenated fat system, the hydrogenated fat will allow a much greater inclusion of cocoa butter before it moves away from stable β'_2 structure into a mixed β_3 - β'_2 system. The effect of this, in practice, is to allow a greater inclusion of cocoa butter into these types of substitute coating.

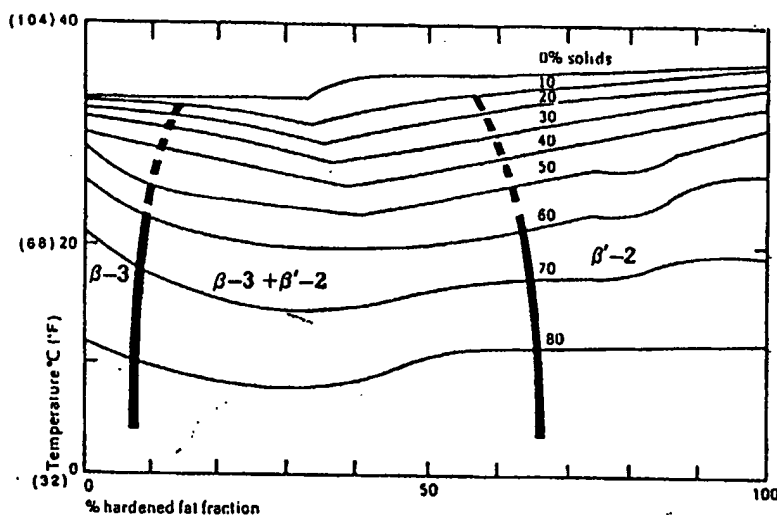


Figure 7.11 Iso-solids phase diagram of cocoa butter-hydrogenated non-lauric fat. (Reprinted with permission of Loders Croklaan.)

7.8 Migration of fats in composite products (see also chapter 21)

Many products consist of one phase containing a hard fat adjacent to a second phase containing a softer fat. One of the problems associated with products like these is that the softer, more mobile, fat can migrate into the harder fat. Thus, the interactions between the two fats can be of importance in determining, at a practical level, the shelf-life and consumer acceptance of the product, and at a more fundamental level, the crystal structure and melting profile of the product.

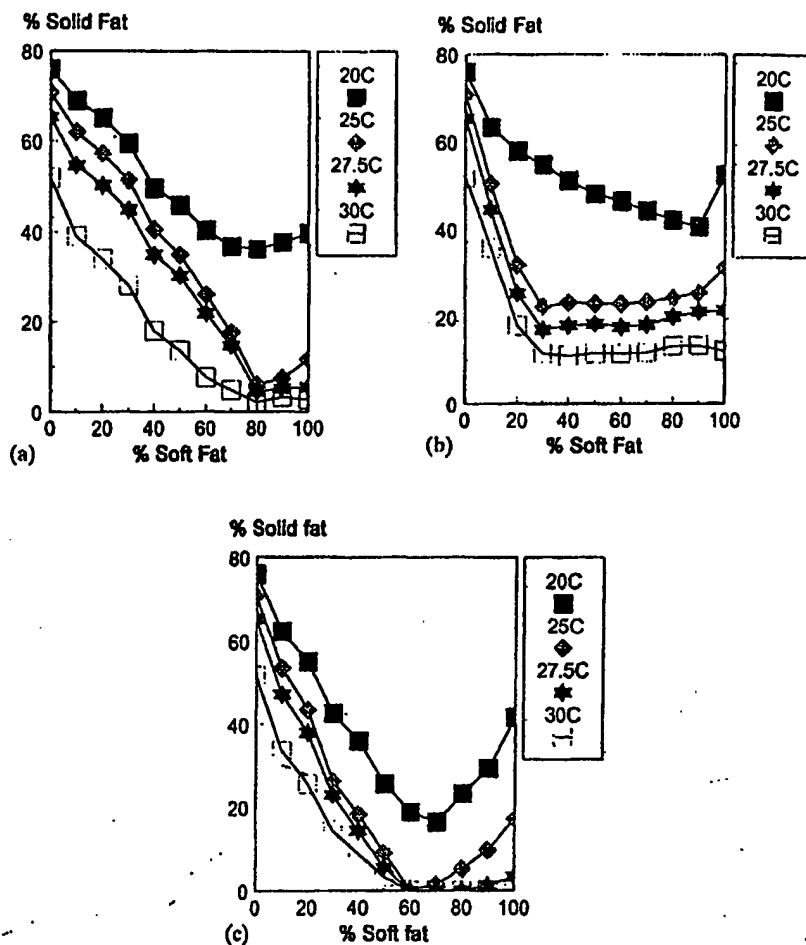


Figure 7.12. Interactions of cocoa butter with soft fats. (Reprinted with permission of Lodders Crocklaan.) (a) Soft β -stable fat. (b) Soft β' -stable non-lauric fat. (c) Soft β' -stable lauric fat.

(see also chapter 21)

the problems associated with mobile, fat can migrate into the two fats can be of the shelf-life and consumer fundamental level, the crystal

Distinction has already been made between β -stable, cocoa butter-like fats, β' -stable lauric fats and β'' -stable non-lauric fats. Using that distinction, the practical interactions between all possible pairs of these three groups will be examined [24].

The three 'hard fats' are (a) cocoa butter, (b) a fractionated lauric fat and (c) a hydrogenated and fractionated non-lauric fat. The three 'soft fats' are (a) a β -stable, i.e. cocoa butter-like soft fat, (b) palm kernel oil and (c) a soft hydrogenated, fractionated non-lauric fat. The interactions

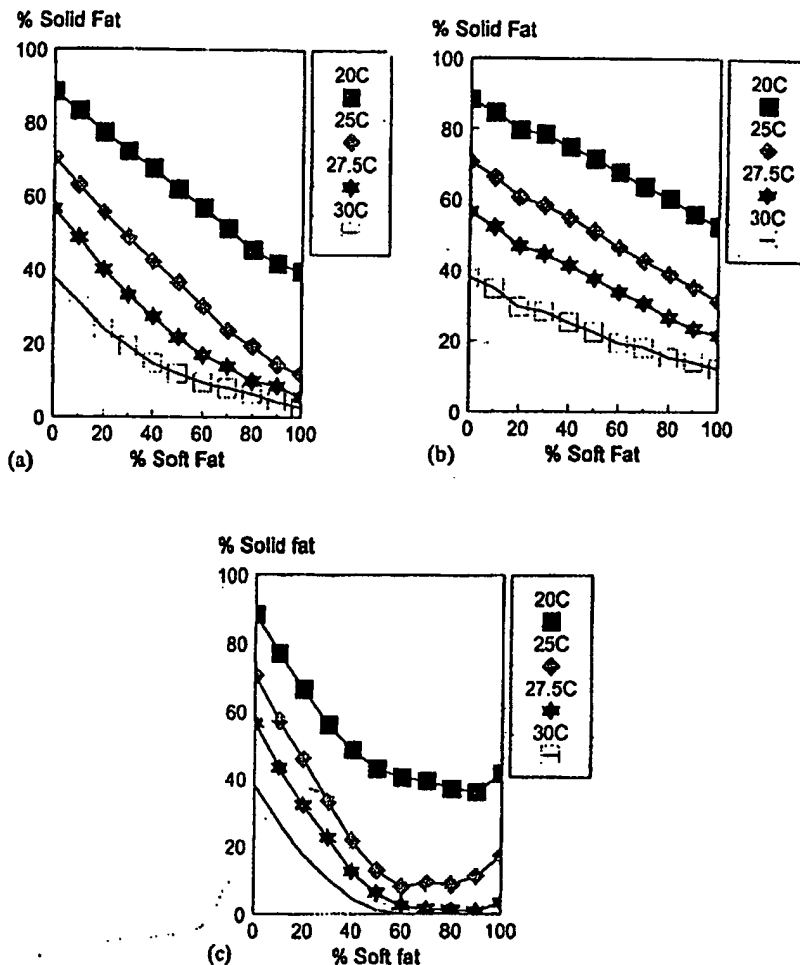
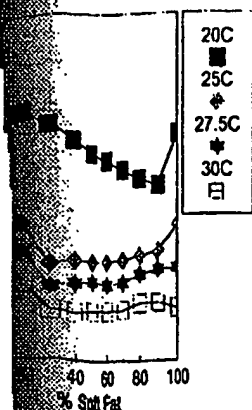


Figure 7.13 Interactions of a hydrogenated non-lauric coating fat with soft fats. (Reprinted with permission of Loders Crokiaan.) (a) Soft β -stable fat. (b) Soft β -stable non-lauric fat. (c) Soft β -stable lauric fat.

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Springer-Verlag. (c) Soft β' -stable

between each of the three soft fats and cocoa butter are shown in Figure 7.12. When cocoa butter is mixed with a softer, but still, β -stable fat, a slight eutectic is observed at about 20% cocoa butter. Between 100% and 20% cocoa butter, the decrease in solid fat content is fairly linear; between 20% and 0% cocoa butter, a slight rise in solid fat contents at 20°C and 25°C (68°F and 77°F) is observed.

The interactions between cocoa butter and a soft hydrogenated non-lauric fat show distinct phase differences. Between 100% and 70% cocoa

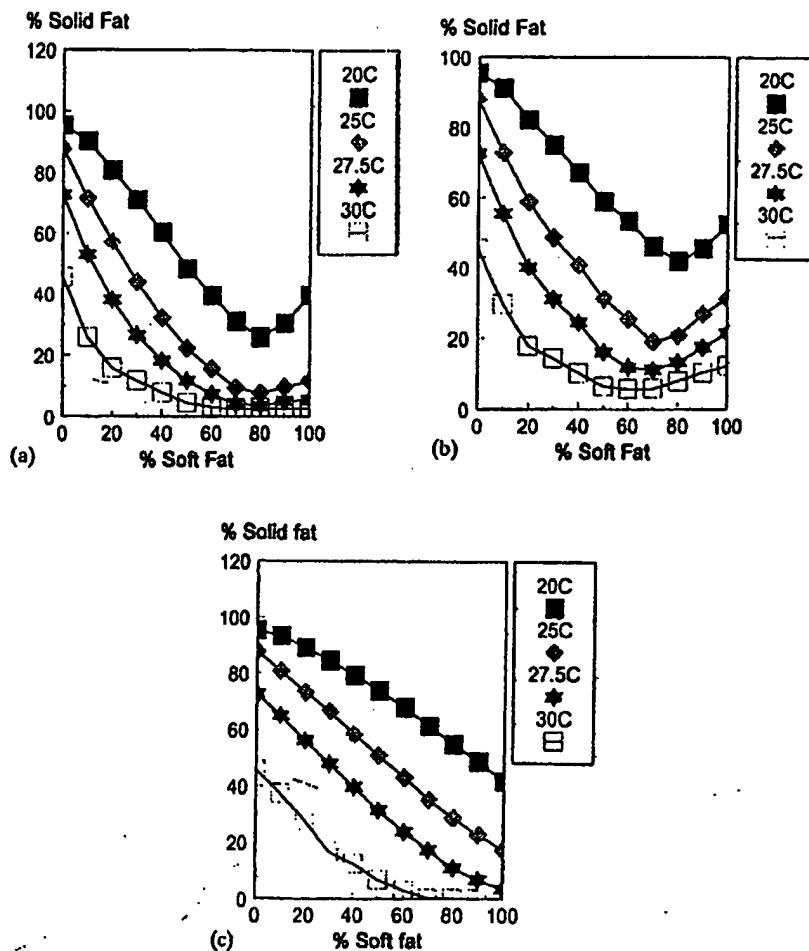
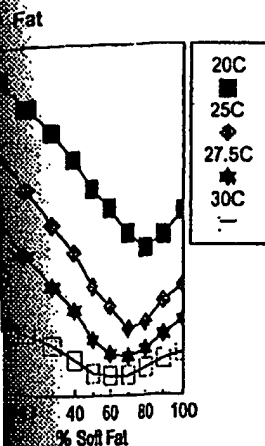


Figure 7.14 Interactions of a hydrogenated lauric coating fat with soft fats. (Reprinted with permission of Lodders Croklaan.) (a) Soft β -stable fat. (b) Soft β' -stable non-lauric fat. (c) Soft β' -stable lauric fat.

cocoa butter are shown in Figure 7.12. The solid fat content of cocoa butter, after, but still, β -stable fat, a cocoa butter. Between 100% and 70% soft fat, the solid fat content is fairly linear; between 70% and 50% soft fat, the solid fat content is fairly linear; between 50% and 30% soft fat, the solid fat content is fairly linear; between 30% and 10% soft fat, the solid fat content is fairly linear; between 10% and 0% soft fat, the solid fat content is fairly linear.



butter, considerable softening, particularly at 25°C (77°F) and above, is observed as the level of soft fat increases; between 90% and 100% soft fat, an increase in solid fat at 20°C and 25°C (68°F and 77°F) is observed. It is likely, therefore, that phase boundaries exist at about 70% and 10% cocoa butter. Between these phase boundaries the solid fat content, particularly at $\geq 25^\circ\text{C}$ (77°F) is relatively unaffected by differences in composition.

The third case, cocoa butter mixed with a soft lauric fat, shows a deep eutectic at 60–70% soft fat and demonstrates the incompatibility between these two fats.

The interactions between a high-solids, hydrogenated, non-lauric coating fat and three softer fats are shown in Figure 7.13. Here we see that when the soft fat is 'polymorphic' and, particularly, when it is also a hydrogenated, non-lauric fat, the interactions between the hard and soft fats are fairly linear, indicating a good degree of compatibility between the fats. The mixtures with the soft lauric fat, however, again show a eutectic composition between 60% and 90% soft fat (although this is not as pronounced a eutectic as that observed with cocoa butter).

When the hard fat is a hydrogenated lauric coating fat, the interactions are as shown in Figure 7.14. These show eutectics with the β -stable fat and with the hydrogenated non-lauric fat, both at about 70–80% soft fat, but relatively linear mixing with the soft lauric fat.

The compatibilities of fats from these three groups can be summarised as shown in Figure 7.15. When fats from the same basic group are mixed together, the compatibility between them is usually very good. Polymorphic (β -stable) fats and hydrogenated non-lauric fats show a limited (denoted as 'fair') compatibility. Lauric fats have a poor compatibility with any fats, apart from other lauric fats.

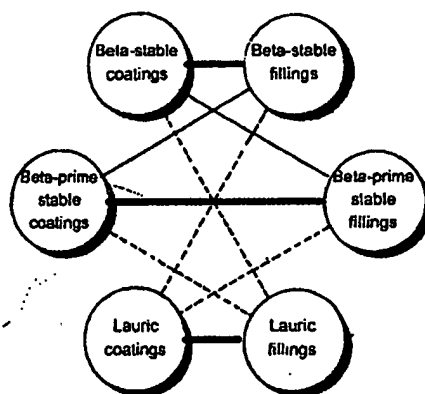


Figure 7.15 Compatibility of fats. (Reprinted with permission of Lodders Crocklaan.)

7.9 Conclusion

The way in which fats crystallise, particularly the polymorphic changes which can take place in a fat, at what may be critical processing temperatures, is of paramount importance in the processing of foods. Equally, as composite foods become more complex, the interactions between fats in the different parts of the food is also critical. This is especially so if the textural differences, which can be so important for consumer acceptability, are to be maintained.

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by wrapping electrical heater tapes round the drums or by progressively lowering steam coils into the fat.

4.2 BORNEO ILLIPÉ (ILLIPÉ-BUTTER, BORNEO TALLOW)

Borneo illipé fat is extracted from nuts of the *shorea* tree found in the forests of Borneo. Following collection the nuts are dried before shipment to the processing plant.

The colour varies from white to pale green. It has properties which closely resemble those of cocoa butter, completely melting at 37°-38° C (99°-100° F). The fatty acid composition is very simple, consisting of stearic, oleic and palmitic acids. On cooling, the fat crystals form at a lower temperature than those which form in cocoa butter treated under similar conditions. Borneo illipé is harder than cocoa butter and the fat can be used to improve the handling properties of chocolate products such as Easter eggs. The incorporation of Borneo illipé in chocolate raises the melting point and improves the storage resistance, particularly when manufactured for the tropics.

The temperature range used for tempering chocolate should be raised if illipé butter is incorporated.

4.3 COCONUT OIL

Coconut oil is extracted from the fruit of the coconut palm grown in West Africa, India, Ceylon and the Philippines. After drying, the oil is extracted from the flesh of the nut. The composition of the oil varies according to the processing method.

The fat has a brittle texture and may vary from cream to deep yellow brown in colour. It has a clear melting point at 25° C (77° F). Refining removes much of the colouring matter and most of the coconut flavour present in the raw material.

Coconut oil can be selectively hydrogenated to raise the melting point and stability of the fat. Completely hydrogenated coconut oil melts at 35° C (95° F).

4.4 GROUNDNUT OIL (PEANUT OIL, EARTHNUT OIL)

This is extracted from the nuts removed from the pods of the groundnut plant. The oil content of the groundnut is 45-48% depending on source: the extracted unrefined oil varies in colour from yellow to brown and is nutty in taste.

The extractable fatty material, after refining, sets at 0° C. As the temperature approaches freezing point, a crystalline sediment of stearines develop in the oil. The fatty acid composition of the oil varies according to source, the major acids being oleic and linoleic. Groundnut oil is quite